Phonon Model of Vacancy-Interstitial Pair Formation in Solids

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Bonds between neighboring atoms in a solid are imperfect harmonic oscillators. Through consideration of the nonlinearities, it is shown that vacancy-interstitial defect pairs can be described in terms of phonon dynamical variables. The effective spring constants are determined by self-consistency requirements. An inhomogeneous solution is found to the equations of the self-consistent spring constants; it describes an atom breaking its bonds to its neighbors, resulting in a defect pair.

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The usual picture of a vacancy starts with an atom in a potential well of depth V_0 due to its neighbors. When the Boltzmann factor $\exp(-V_0/kT)$ becomes appreciable, the atom is capable of jumping out of the well, becoming an interstitital (atom), and leaving behind a vacancy.[1] Although the two defects can recombine, they both have significant diffusion coefficients and, therefore, a finite probability of breaking apart.

While this picture is reasonable, it is flawed. The natural description of the motion of an atom in a previously homogeneous solid has to involve the collective phonon modes, even though the potentials are only approximately harmonic. Our procedure is to examine the small oscillations about self-consistent solutions. We find that there is a homogeneous solution which maintains the point-group and translational symmetries found at $T=0$. But the partition function also has contributions from symmetry-broken collective states, in which a small fraction of the atoms acquire a large amplitude of motion, sufficient for the creation of defects. The process by which this occurs can be understood without much calculation. The present paper is intended to be an introduction into the topic, while detailed applications to real solids are relegated to future publications. However, before turning to the study of defects, let us examine the homogeneous solid to see why an excited large-amplitude solution which is also found in this situation must be discarded.

Homogeneous lattice.—The homogeneous case serves to illustrate the methodology, which is a generalization of the "quasiharmonic approximation" used in the study of anharmonic solids.[2] We start by defining an effective temperature-dependent interatomic potential function $V_T(\xi)$, having depth W_0 and an effective spring constant (curvature) $K_{\rm eff}$, by performing thermal averages (denoted by $\langle\cdots\rangle$) over the bonds connecting each atom at R_i to its z nearest neighbors at $R_{i+\delta}$:

$$V_T(\xi)=\frac{1}{z}\sum_{\delta=1}^{z}\langle V(R_i-R_{i+\delta}-R_i^0+R_{i+\delta}^0+\xi)\rangle,$$
$$=W_0+\tfrac{1}{2}K_{\rm eff}\xi^2+\cdots. \quad (1)$$

W_0 is a measure of the average potential energy; $K_{\rm eff}$, of the (thermally averaged) restoring forces. While the former increases with T, the latter generally decreases. Although exceptions may be found for certain complicated potential functions, the prototype shallow-well Gaussian potential demonstrates such features nicely. We take it of the form

$$V(r)=\tfrac{1}{8}K_0a_0^2\{1-\exp[-(2r/a_0)^2]\}, \quad (2)$$

with a_0 the presumed equilibrium lattice constant, and r the deviation of the bond length from its optimal value. Let us apply the same analysis which successfully explains the Debye-Waller factor in x-ray scattering,[3] and examine the Fourier components:

$$\exp[-(2r/a_0)^2]$$
$$=a_0(4\pi)^{-1/2}\int_{-\infty}^{\infty}dk\,e^{ikr}e^{-(ka_0/4)^2}. \quad (3)$$

Then, the appropriate V_T in this case is

$$V_T(\xi)=\langle V(r+\xi)\rangle=\tfrac{1}{8}K_0a_0^2\{1-a_0(4\pi)^{-1/2}\int dk\,\langle e^{ikr}\rangle e^{ik\xi}e^{-(ka_0/4)^2}\}, \quad (4)$$

where[3]

$$\langle e^{ikr}\rangle=\exp(-\tfrac{1}{2}k^2\langle r^2\rangle). \quad (5)$$

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The thermal motions $\langle r^2\rangle$, the phonon potential energy $u(T,y)$ stored in the bond under examination, and the effective spring constant $K_{\rm eff}$ are related as follows:

$$u(T,y)=\tfrac{1}{2}K_{\rm eff}\langle r^2\rangle. \tag{6}$$

The Debye theory yields an explicit expression for $u(T,y)$ which we find useful:

$$u(T,y)=\tfrac{1}{2}kTD(\theta_0/Ty)+\tfrac{3}{16}k\theta_0/y, \tag{7}$$

where θ_0 is the Debye temperature of the lattice in question with all spring constants K_0, and y takes explicit account of the fact that the bonds have weakened to the value $K_{\rm eff}$. As the phonon spectrum scales with $K_{\rm eff}^{1/2}$, we have used θ_0/y in (7) instead of the usual θ_0, defining

$$y=[K_0/K_{\rm eff}]^{1/2}. \tag{8}$$

The Debye function $D(x)$ is the tabulated function[4]

$$D(x)=(3/x^3)\int_0^x dt\, t^3(e^t-1)^{-1}, \tag{9}$$

which has the following limiting values:

$$D(x)\sim \pi^4/5x^3, \quad x\gg 1, \qquad D(x)\sim 1, \quad x\ll 1. \tag{9a}$$

To obtain $K_{\rm eff}$ or, what is equivalent, y, we evaluate (4):

$$V_T(\xi)=\tfrac{1}{8}K_0a_0^2\{1-g(T)\exp(-[2g(T)\xi/a_0]^2)\}, \tag{10}$$

where we have defined a useful auxilliary quantity $g(T,y)$:

$$g(T,y)\equiv[1+8\langle(r/a_0)^2\rangle]^{-1/2}. \tag{11}$$

By (6)–(8) we can determine $g(T,y)$ in terms of T and y explicitly. On the other hand, expansion of V_T in powers of ξ^2 yields expressions for the effective potential depth,

$$W_0=\tfrac{1}{8}K_0a_0^2[1-g(T)], \tag{12}$$

and for the spring constant $K_{\rm eff}\equiv K_0y^{-2}$,

$$K_{\rm eff}=y^{-2}K_0=K_0g^3(T,y). \tag{13}$$

So while (11) yields $g(T,y)$ as a function of y, (13) gives y as a function of g. The simultaneous solution of these equations is reducible to the following:

$$y=\left[1+\frac{8uy^2}{\frac{1}{2}K_0a_0^2}\right]^{3/4}, \tag{14}$$

plotted schematically in Fig. 1. This equation either has two solutions, or it has none. We can estimate the temperature T^* above which it has no solution, for solids in which the zero-point motion is not too important, i.e., if $T^*>\theta_0$, by assuming $u(T^*,y^*)$ to have achieved its asymptotic value, $\frac{1}{2}kT^*$. It then follows from some straightforward analysis that

$$kT^*=(0.096\,225)\tfrac{1}{2}K_0a_0^2, \qquad y^*=2.2795. \tag{15}$$

T^* is an upper bound to the sublimation temperature in this model. The value of y^* indicates that once $K_{\rm eff}\lesssim\frac{2}{3}K_0$ no self-consistent quasiharmonic approximation is possible.

Below T^*, if we try to solve (14) by iteration we discover that any $y_{(n)}$ in the range $(0,y_1)$ leads to a value $y_{(n+1)}$,

$$y_{(n+1)}=\left[1+\frac{8u_{(n)}y_{(n)}^2}{\frac{1}{2}K_0a_0^2}\right]^{3/4}, \tag{16}$$

which is closer to the ultimate stable fixed point y_0. y_0 is seen to be the smaller of the two possible solutions. The solution y_1 of Eq. (14) is unstable. It is easy to verify that any $y_{(n)}>y_1$ leads to a $y_{(n+1)}$ which is greater still, leading ultimately to ∞, while any $y_{(n)}$ less than y_1 leads to the stable fixed point at y_0. This behavior, indicated by arrows in Fig. 1, is indicative of the nonlinear dynamics. The stable,

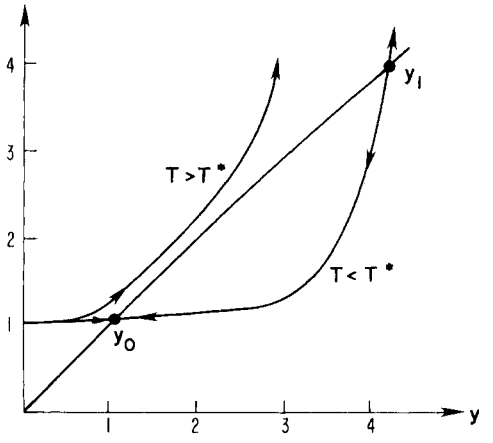

FIG. 1. Schematic solution of Eq. (14) showing stable solution y_0 and unstable solution y_1. At T^* these merge, and above T^*, iteration of Eq. (14) leads to $y=\infty$. Thus, there is no stable self-consistent quasiharmonic solid for $T\geq T^*$.

homogeneous, isotropic solution corresponding to y_0 is stable until it merges with the unstable solution $y_1 = y^*$ at a temperature T^*. Above that, only the gas phase is stable.

The energies corresponding to the various fixed points y_0, y_1, and ∞ are

$$W_0(y_0) = \tfrac{1}{8}K_0a_0^2[1-y_0^{-2/3}], \quad W_0(y_1) = \tfrac{1}{8}K_0a_0^2[1-y_1^{-2/3}], \quad W_0(\infty) = \tfrac{1}{8}K_0a_0^2, \tag{17}$$

in ascending order. These are energies *per* bond. Thus, the Boltzmann factor giving the relative probability of y_1 is

$$P(y_1) = \exp\{-\tfrac{1}{2}Nz[W_0(y_1) - W_0(y_0)]/kT\} = \exp\{-\tfrac{1}{16}K_0a_0^2[y_0^{-2/3} - y_1^{-2/3}]Nz/kT\}, \tag{18}$$

which is effectively zero in the thermodynamic ($N \to \infty$) limit. Consequently, the y_1 solution is prohibited thermodynamically as well as dynamically.

In the next section, we shall see that there is a contribution to the partition function from *isolated* atoms. There is no factor N in the exponents; therefore, these symmetry-broken solutions are present at finite T.

Symmetry breaking.—Suppose a given atom is selected as candidate for a defect. The spring constant $\hat{K}$ connecting it to each of z nearest neighbors is presumed weakened by a common amount relative to the bulk value K_{eff} found in the preceding section.

We can avoid the use of complicated scattering theory for phonons[5] by restricting the analysis to temperatures $T > \theta_0$. By equipartition, the potential energy of the phonons in each defect bond, $\hat{u}$, just equals the bulk values $u(T)$ which itself is approximately $\frac{1}{2}kT$ in this temperature range. Thus, the defect spring parameter and thermal averaged motion are related by

$$\tfrac{1}{2}\hat{K}\langle\hat{r}^2\rangle = \hat{u} \approx u \approx \tfrac{1}{2}kT. \tag{19}$$

We define

$$\hat{y} = (K_{\text{eff}}/\hat{K})^{1/2} \tag{20}$$

as the defect spring parameter. Then the self-consistent equation which replaces (14) takes the form

$$\hat{y}y_0 = \left(1 + \frac{8uy_0^2\hat{y}^2}{\frac{1}{2}K_0a_0^2}\right)^{3/4}. \tag{21}$$

It admits the homogeneous solution $\hat{y} = 1$ trivially, and a second, nontrivial solution,

$$\hat{y}_1 = y_1/y_0, \tag{22}$$

corresponding to the unstable solution in Fig. 1.

Unlike the situation for the homogeneous solid, such localized defects do contribute to the partition function. The energetic cost for each of z broken nearest-neighbor bonds is finite, given in Eq. (17), and we obtain for the relative probability of the creation of a vacancy-interstitial pair about an arbitrary site

$$P_{\text{defect}} = \exp\left[-\frac{z}{16}\frac{K_0a_0^2(y_0^{-2/3} - y_1^{-23})}{kT}\right], \tag{23}$$

which represents, therefore, the concentration of defects. The activation energy for escape is thus

$$V_0 = (z/16)K_0a_0^2(y_0^{-2/3} - y_1^{-2/3}), \tag{24}$$

temperature-dependent quantity. Its calculation from Eq. (14) supplies a microscopic basis for the quantity V_0 mentioned in the introductory paragraph. We should not rely on such expressions near T^*, where $V_0 \to 0$, for there the interaction among defects would play an important role. However, it is expected that melting usually occurs at a temperature $T_m < T^*$. If the density of vacancies at T_m is still low, the above should give a reasonable account of it.

In summary, we have found a description of nonlinear phenomena such as the formation of defect pairs using the familiar formalism of phonons. This requires the use of collective parameters $\hat{K}$ or K_{eff} which are determined self-consistently. In future work, we intend to show how these are related to other properties of the solid.

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[1]See discussion in almost any solid-state textbook, *inter alia*, C. A. Wert and R. M. Thomson, *Physics of Solids* (McGraw-Hill, New York, 1964), Chap. 3; also, O. Madelung, *Introduction to Solid State Theory* (Springer, Berlin, 1978), and J. Ziman, *Principles of the Theory of Solids* (Cambridge, Univ. Press. Cambridge, England,

1964).

[2]Madelung, Ref. 1; quasiharmonic approximation: p. 320ff; Debye temperature: p. 142.

[3]Ziman, Ref. 1, p. 60ff. Put briefly, the contribution to the exponential is a sum over N normal modes each of which contributes $O(1/N)$. The result, according to the central limit theorem, is a Gaussian.

[4]M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1964), p. 998.

[5]See, for example, the various reprints in A. A. Maradudin *et al.*, *Lattice Dynamics* (Benjamin, New York, 1969). I thank my colleague, Dr. B. G. Dick, for this reference.